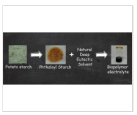
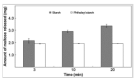
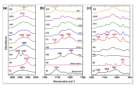
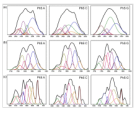
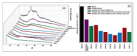


Table 1









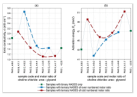


Table 2

Carbohydrate Polymers

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Ternary natural deep eutectic solvent (NADES) infused phthaloyl starch as cost efficient quasi-solid gel polymer electrolyte

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Highlights

- Starch was modified via phthaloylation prior to polymer electrolyte fabrication.
- Inclusion of urea in NADES improves the conductivity and physical properties of the gel.
- Highest ionic conductivity of 2.86 mS cm^{-1} was achieved.

Abstract

A first-of-its-kind, eco-friendly quasi-solid bioelectrolyte derived from potato starch was prepared. Starch was chemically modified via phthaloylation to synthesize amorphous, hydrophobic starch derivative and the attachment of the phthaloyl group was confirmed via FTIR which showed phthalate ester peak at 1715 cm^{-1}; and ^{1}H NMR peaks between 7.30–7.90 ppm attributed to the aromatic protons of the phthaloyl group. The resulting starch derivative was then infused with ternary natural deep eutectic solvent (NADES) made from different molar ratios of choline chloride, urea and glycerol. Electrochemical Impedance Spectroscopy (EIS) revealed that the highest ionic conductivity was obtained by the system consisting of NADES with choline chloride:urea:glycerol in molar ratios of 4:6:2, with a magnitude of 2.86 mS cm^{-1}, hence validating the prospects of the materials to be further experimented as an alternative electrolyte in various electrochemical devices.

Graphical abstract

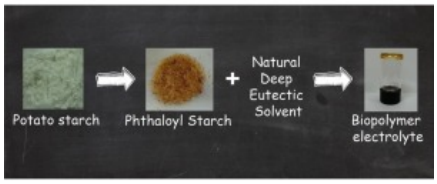

Figure options

Keywords

Starch; Polymer electrolyte; NADES; Phthaloylation; Ionic conductivity

1. Introduction

Fabrication of starch based polymer electrolytes is currently an active area of research in electrochemistry. This category of electrolyte is especially appreciated for its cost efficiency, biodegradability and natural abundance, hence qualifying them as excellent substitutes to the conventional petroleum based polymer electrolytes (Manuel Stephan, 2006). However, the high crystallinity of starch in its natural state inhibits flexibility of the polymer chain and thus prevents the electrolyte from achieving high ionic conductivity. The high hydrophilicity of pristine starch also prevents it from being dissolved in most organic solvents and this limits the preparation of starch electrolyte to only solid films. Previously, phthaloylation of polysaccharides such as chitosan have been shown to be successful in imparting organosolubility and suppressing crystallinity (Yusuf et al., 2016). High ionic conductivity was achieved when this modified chitosan was used as the host in the fabrication of gel polymer electrolyte (Azzahari, Yusuf, Selvanathan, & Yahya, 2016). Thus, in this study, the hydrophilic and crystalline properties of pristine starch are reformed via a simple phthaloylation reaction and used as a component to fabricate a novel quasi-solid bioelectrolyte based on the starch derivative.

In recent times, quasi-solid polymer electrolytes are emerging as a unique class of electrolytes; highly celebrated for its good physical stability and high ionic conductivity. Conventionally, the fabrication of quasi-solid gel polymer electrolyte is achieved by incorporating organic solvents and lithium or sodium based ionic salts into the polymer host (Di Noto, Lavina, Giffin, Negro, & Scrosati, 2011; Hallinan and Balsara, 2013 ; Manuel Stephan, 2006). Recently, the inclusion of imidazolium based ionic liquids was also performed in preparing gel electrolytes with high ionic conductivities (Karuppasamy et al., 2016; Ortega, Trigueiro, Silva, & Lavall, 2016). However, such approach elevates the preparation cost while at the same time threatens the biodegradability of the electrolyte.

Deep eutectic solvents (DES) are gaining vast attention since they exhibit similar physico-chemical properties to traditional imidazolium based ionic liquids and therefore advantageously replace them in many applications. The low ecological footprint, ease of preparation and economical price of deep eutectic solvents as compared to ionic liquids could promote their usage on a large-scale (Zhang, De Oliveira Vigier, Royer, & Jerome, 2012; Dai, van Spronsen, Witkamp, Verpoorte, & Choi, 2013). In this study, a specific group of DES known as natural deep eutectic solvent (NADES), which is obtained from a wide range of natural compounds including amines, amino acids, alcohols, carbohydrates and carboxylic acids, have been employed as the solvent (Pena-Pereira, Kloskowski, & Namiesnik, 2015). Besides its biocompatibility, NADES were found to exhibit excellent solubilizing capabilities for a range of both polar and non-polar small molecules and macromolecules (Dai et al., 2013; Dai, Verpoorte, & Choi, 2014; Pena-Pereira et al., 2015). Hence, the starch derivative is infused with NADES comprising of choline chloride, as the quaternary ammonium salt, with urea and glycerol, as the hydrogen bond donors.

To date, NADES have only been used as the plasticizing agents in starch and cellulose based films, (Ramesh, Shanti, & Morris, 2012; Ramesh, Shanti, & Morris, 2013). However, this is the first attempt in which ternary deep eutectic solvents have been employed as the solvent in the electrolyte composition. Since the starch gel electrolyte contains ionic carrier and plasticizer components within its solvent system, this eradicates the need to include any additional plasticizers or salts.

According to Maugeri and de Maria, addition of glycerol as a third component into binary DES resulted in reduced viscosity of the ternary DES (Maugeri & Dominguez de Maria, 2012). Since lower viscosity translates into higher conductivity, this observation inspired us to explore the effect of varying the glycerol content in the ternary NADES on the ionic conductivity of the polymer electrolyte.

2. Materials and methods

2.1. Materials

Potato starch was purchased from Omya Hamburg. Urea, choline chloride, and glycerol were procured from Sigma Aldrich. Phthalic anhydride, pyridine, dimethylformamide

(DMF), isopropanol, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Merck. *Bacillus licheniformis* α-amylase (BLA) (lot 018K7018V) and 3,5-dinitrosalicyclic acid (DNS) were supplied by Sigma-Aldrich Co., USA. Maltose was obtained from R & M Chemicals, UK. All materials were used as received.

2.2. Preparation of polymer electrolyte

2.2.1. Phthaloylation of starch

10 g of starch was suspended into a flask containing 60 mL of DMF and heated up to 80 °C under heterogenous condition with constant stirring. After 30 min, 18.5 g of phthalic anhydride and 8 g of pyridine was then added to the mixture, and the reaction was allowed to proceed at the same temperature for another 4 h. The phthaloylated starch product which was now in a homogenous solution, was then retrieved by precipitation with isopropanol and dried under vacuum at 80 °C until constant weight. The degree of substitution of the esterified starch was determined by the back titration method (Stojanović, Jeremić, Jovanović, & Lechner, 2005) (Note 1, Supplementary data).